Detectors: Selective

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Introduction

The packed columns used in the early days of GC were inefficient by modern standards and so selective detectors that only gave a response to particular elements or compounds had obvious advantages when analysing complex mixtures. There was also a big incentive to develop more sensitive detectors and the detection of an organic vapour in an inert gas lent itself to the development of a host of devices, the majority of which have failed to make any lasting impact. Even today when the mass spectrometer is the selective detector *par excellence* there are still a number of other, more limited, detectors commercially available and this situation seems likely to continue. This paper describes some of these detectors; it should be noted that they are described as 'selective' rather than 'specific' since although they may give a large signal for one type of analyte they will also invariably give a small signal for others.

In general, selective detectors usually have more operating parameters than the two common universal detectors, the thermal conductivity detector (TCD) and the flame ionization detector (FID), and are more sensitive to small changes in these parameters. Some selective detectors are so temperamental that, having needed several days to set them up, they are then best left in continuous standby even when not in use.

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Element-Selective Detectors

Although there are selective detectors for most elements, the common ones are those for sulfur, nitrogen, phosphorus and the halogens. These elements account for the great majority of published work because they are the ones most likely to be encountered in most real life applications.

Sulfur-Selective Detectors

Sulfur is an important element which turns up in many fields usually with deleterious effects; 0.1 ppm of a mercaptan in isopropyl alcohol would, for example, render it totally unfit for perfumery applications.

The flame photometric detector (FPD) monitors the light emitted by a hydrogen-rich 'cold' flame. Under these conditions sulfur (the S_2 species) has a band spectrum with a maximum at 394 nm and phosphorus (HPO) has a band spectrum with a maximum at about 526 nm. Since these are band spectra they do not exhibit the very sharp emission lines of atomic spectra and are, therefore, only moderately selective. There are carbon band spectra, for example at 388 nm, that tend to interfere with the sulfur spectrum. The response is approximately equimolar for different sulfur compounds unless oxygen is also present in the molecule. Since it is an S_2 species being monitored in the flame the response is approximately proportional to the square root of the concentration. This disadvantage can be catered for by suitable electronics but there is always some doubt about whether the response follows the square root relationship accurately and calibration is essential for reliable quantitative results. Another severe disadvantage of the simple FPD is that co-eluted organic compounds not containing sulfur will 'quench' the sulfur emission and cause a drastic diminution of signal.

In spite of these disadvantages the FPD has proved a popular and important detector especially in the food and petroleum industries. For example, in the former it has been used for the detection of mercaptans in lager. In the latter it has been shown that a crude oil, so biodegraded that it can no longer be identified by its hydrocarbon fingerprint, can still be recognized by its sulfur fingerprint since the sulfur compounds are much more slowly degraded.

There have been a number of attempts over the years to improve the performance of the FPD. A dual-flame version oxidizes the sulfur compounds to SO_x in an ordinary oxidizing flame and the products of combustion are then taken to the hydrogen-rich cold flame. This gives a considerable reduction in the quenching effect of co-eluting compounds but at the cost of at least 10-fold loss in sensitivity from about $10^{-9}\,g\,s^{-1}$ for the single flame version. Another version, the pulsed FPD, developed by Amirav *et al.* in 1991, reduced the hydrogen flow rate so that the flame is extinguished and re-ignited about 2–4 times a second. The emission during each period of emission is scanned from the time of ignition and electronically time-gated. Under these conditions it is possible to discriminate on a time basis between carbon emissions taking place at 2–3 ms after ignition and sulfur emissions which take place at about 6 ms. Thus with this design there is both wavelength and time discrimination and the combined effect is a very high selectivity and a sub-picogram per second sensitivity. In spite of these advantages there are few publications on the use of the PFPD to date.

Most versions of the FPD can be used for phosphorus detection by changing the filter from 394 nm for S to 526 nm for P and a number of other elements such as Se, Sn, As and Ge have also been determined at various wavelengths and with varying degrees of selectivity and sensitivity. Simultaneous detection of two elements is also possible.

A different type of sulfur/nitrogen selective detector has been successfully developed in the last few years. In the sulfur chemiluminescence detector (SCD), the sulfur-containing compounds are combusted in an oxidizing flame or in later versions in a miniature ceramic furnace to SO_x which is then reacted with ozone in a low pressure chamber at about 10–15 Torr. Reaction with ozone raises the sulfur oxides to an excited state and as the molecules drop back to the ground state they emit light in the far blue end of the spectrum which is monitored by a photomultiplier tube after passing through an optical filter. Sub-picogram per second sensitivity is claimed for this detector with a linear response over five orders of magnitude, equimolar response for different sulfur compounds and no quenching effects. By replacing the optical filter for sulfur with one in the red region (610 nm) the detector can be used selectively for nitrogen. This is, in effect, similar to the so-called Thermal Energy Analyser™ which was produced in the 1970s specifically for the analysis of nitrosamines in food but which never achieved wide popularity.

Figures 1A–D show chromatograms of a gas oil before and after a hydrotreater unit designed to reduce the total sulfur content of the fuel from about 220 ppm to 2 ppm. Figures 1A and B show the before and after FID traces where it is difficult to see any difference and Figures 1C and D show the before and after SCD chromatograms where the difference is clearly apparent.

Nitrogen-Selective Detectors

To a certain extent these have been covered in the section above but the commonest nitrogen-selective detector is the flame thermionic detector. This is abbreviated to FTD or NPD, since by operating under different conditions the detector can be made selective for nitrogen or phosphorus (but not both simultaneously). Like the FPD this detector has a long history of development originating in the observation that alkali metal compounds introduced into a flame gave a high response for halogens. Indeed, early detectors were made by modifying leak detectors used to monitor the escape of halogenated gases from refrigeration units. By operating under different conditions, selectivity for nitrogen and phosphorus could also be obtained. The next development was to use a small flame as in an FID to impinge upon a pellet of an alkali metal salt; later versions had an alkali metal salt flame tip. All these versions suffered from the fact that, as the salt was gradually vaporized in the flame, the response of the detector altered and consequently required frequent calibration. The current version looks very similar to a conventional FID in construction but has a bead of rubidium glass that can be electrically heated to 600–800°C between the flame jet and the main collector electrode. This acts in a somewhat analogous manner to the grid in an electronic triode valve. Since the bead does not depend on a combustion flame for heating it is more stable and less susceptible to variations in response. For nitrogen the hydrogen gas supply to the detector is very small (about 4 mL min^{-1}) and the area of reaction is described as a hydrogen plasma rather than a flame. Increasing the hydrogen flow rate to the flame to about 30 mL min^{-1} increases the sensitivity for phosphorus and reduces the nitrogen response. Typical performance characteristics for the NPD are shown in **Table 1**.

There is still considerable controversy about the mechanism of response of the NPD and for an in-depth discussion of this the reader should consult Patterson (see Further Reading).

The NPD is capable of giving excellent results if used by a skilled operator and it has been used in the nitrogen mode for a wide variety of samples. However, the difficulties in its use for routine analysis and the alternative detectors now available seem to indicate a decline in its use in the future.

Figure 2A shows an FID chromatogram of a sample containing 2 ng amounts of cocaine and heroin and Figure 2B shows the equivalent chromatogram obtained with an NPD. The improved sensitivity and selectivity of the NPD are clearly demonstrated.

Multi-Element Selective Detectors

There are at least two detectors commercially available that are capable of multi-element detection. The first of these is the electrolytic conductivity detector (ELCD), sometimes known as the Hall detector after its main developer and the second is the microwave plasma detector.

The Electrolytic Conductivity Detector (ELCD)

This detector can be used for halogens, nitrogen and sulfur but not for all three simultaneously. The principle of operation of the ELCD is extremely simple. The gases eluting from the column are passed with hydrogen through a small nickel furnace heated to

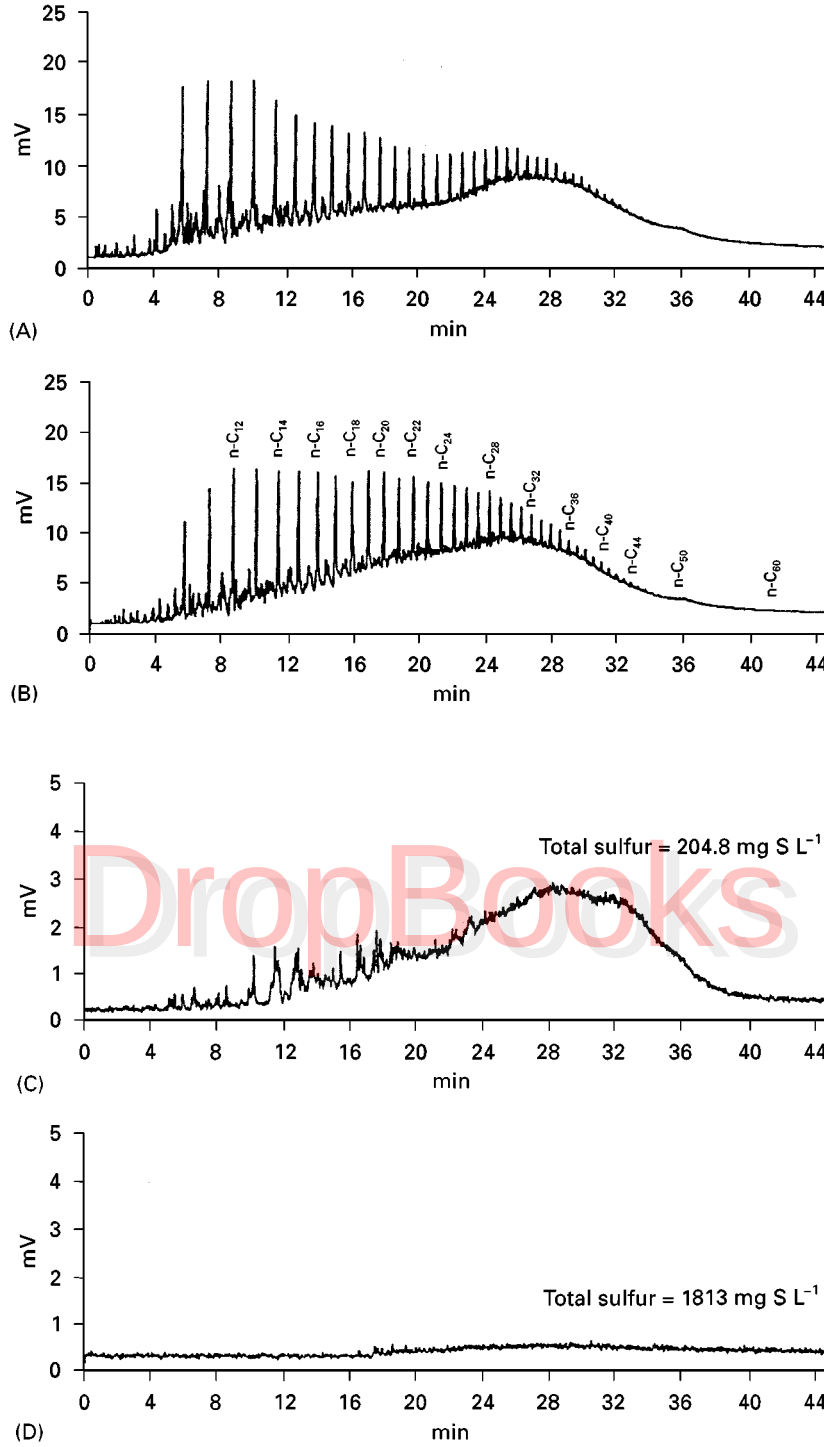

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Figure 1 FID chromatograms of gas oil before (A) and after (B) hydrotreating. SCD chromatograms of gas oil before (C) and after (D) hydrotreating. (From Hutte RS. In *Chromatography in the Petroleum Industry* (1995) Adlard ER (ed.). Reproduced with permission of Elsevier Science.)

about 850–1000°C. Under these conditions halogen compounds are reduced to HX, nitrogen compounds to NH_3 and sulfur compounds to H_2S. These gases are all very soluble in water and if they are passed into a circulating water stream the electrical conductivity will show major changes as the gases emerge. It is also possible to operate in an oxidizing mode so that sulfur goes to SO_x, halogens to HX and nitrogen to N_2.

In practice the equipment is complicated by the fact that the system outlined above would give an integral

Table 1 Typical performance characteristics for the NPD

Characteristic	*Typical values*
Sensitivity	$S_N = 0.1–1.0$ A·s/g N $S_P = 1.0–10.0$ A·s/g P
Detectivity	$D_N = 5 \times 10^{-14}–2 \times 10^{-13}$ g N s^{-1} $D_P = 1 \times 10^{-14}–2 \times 10^{-13}$ g P s^{-1}
Specificity	$S_N/S_C = 10^3–10^5$ gC/gN $S_P/S_C = 10^4–5 \times 10^5$ gC/gP $S_N/S_P = 0.1–0.5$ gP/gN
Linear range	$10^3–10^5$

Source: From PL Patterson in *Detectors for Capillary Chromatography* (eds. HH Hill and DG McMinn). Reproduced courtesy of John Wiley and Sons Inc.

chromatogram rather than the more familiar differential chromatogram and this is overcome by circulating the electrolyte through ion exchange resins to constantly regenerate pure electrolyte. Selectivity for halogens co-emerging with nitrogen or sulfur compounds can be obtained by using other electrolytes rather than water (n-propanol is recommended since other reaction gases are not soluble in it). Another way to obtain selectivity is to use small scrubbers containing chemicals that will remove specific gases. For example an acidic scrubber removes ammonia but allow halogen acids to pass through.

Clearly there are number of opportunities for variation in the chemistries involved (material of reaction tube construction, reaction tube temperature, oxidation or reduction, electrolyte and scrubber) in order to obtain optimum sensitivity and selectivity. For halogens the sensitivity is in the low picogram range with a linearity of five orders of magnitude and a halogen/hydrocarbon selectivity of better than 10^6. In spite of these impressive performance figures the main use of the ELCD has been in the determination of halogenated compounds in water where its use is specified in US Environmental Protection Agency Method 502.2. **Figure 3** shows a chromatogram obtained by purge and trap sampling of water with the ELCD in the halogen mode.

Like the NPD it seems probable that the application of this detector will decline in the future. As separations tend to become faster it is doubtful if the ELCD is capable of providing the rapid response and low dead volume required in such circumstances.

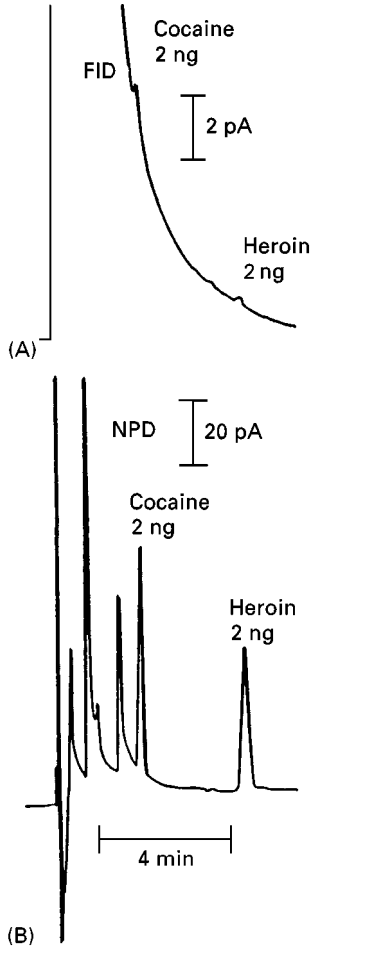
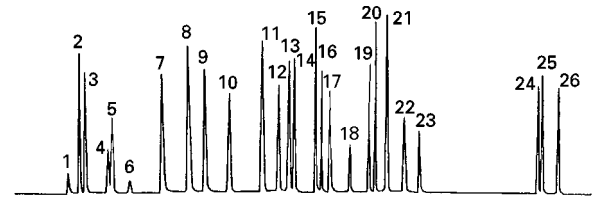


Figure 2 Comparison of FID and NPD chromatograms for a sample containing trace amounts of cocaine and heroin. (From Patterson PL. In *Detectors for Capillary Chromatography* (1992) Hill HH and McMinn DG (eds). Reproduced with permission of John Wiley & Sons, Inc.)



1. Dichlorodifluoromethane
2. Chloromethane
3. Vinylchloride
4. Bromomethane
5. Chloroethane
6. Trichlorofluoromethane
7. 1,1-Dichloroethane
8. Methylene chloride
9. *trans*-1,2-Dichloroethane
10. Chloroform
11. 1,1,1-Trichloroethane
12. Carbon tetrachloride
13. 1,2-Dichloroethane
14. Trichloroethane
15. 1,2-Dichloropropane
16. Bromodichloromethane
17. *cis*-1,3-Dichloropropene
18. *trans*-1,3-Dichloropropene
19. 1,1,2-Trichloroethane
20. Tetrachloroethane
21. 1,2-Dibromoethane
22. Chlorobenzene
23. Bromoform
24. 1,3-Dichlorobenzene
25. 1,4-Dichlorobenzene
26. 1,2-Dichlorobenzene

Figure 3 Chromatogram obtained by purge and trap sampling of water with the ELCD in the halogen mode. (From Hall RC. In *Detectors for Capillary Chromatography* (1992) Hill HH and McMinn DG (eds.). Reproduced with permission of John Wiley & Sons, Inc.) Column: Restek 502.2 FS 0.53 mm × 105 M. Program: 35°C for 11 min, 5°C min^{-1} to 160°C, 4-min final hold. Carrier: helium at 8 mL min^{-1}. ELCD conditions: reactor temperature, 960°C; electrolyte, 35 μL min^{-1} n-propyl alchohol; reaction gas, 100 mL min^{-1} H_2.

The Atomic Emission Detector (AED)

Most of the detectors described above can be used selectively for several elements but this is normally carried out one element at a time, although the FPD, for example, can determine at least two elements (S and P) simultaneously if desired. One of the advantages of the AED is that theoretically it can detect a large number of elements simultaneously with high sensitivity and selectivity. In practice the number determined simultaneously is usually limited to four and, since one of these is normally a carbon channel, only three other elements can be determined.

In the AED, or microwave plasma detector, the compounds are subjected to a high energy microwave plasma so that the emitted spectra are line spectra which are of an extremely narrow wavelength, often only 0.1 Å wide. This results in (potentially) a much higher selectivity and sensitivity.

The AED had a long history of development. It first appeared commercially in the early 1970s. This detector was operated with a microwave plasma in pure helium at low pressure (10–100 mm) and made use of a nitrogen purge to remove carbon deposits from the wall of the silica discharge tube at the outlet of the column. The emission spectra were resolved with a conventional $\frac{3}{4}$m optical spectrometer which resulted in a rather large and unwieldy apparatus which was also sensitive to movement, requiring fairly frequent realignment of the optics. One of the claimed advantages of this detector was that is was possible to obtain the carbon, hydrogen and other element contents of an unknown molecule and so calculate an empirical formula. In practice it was found to give an empirical formula for low molecular weight compounds that was accurate to about $\pm$ 10% and the equipment was never really seriously used for this purpose. Sensitivity and selectivity varied considerably from one element to another. In favourable cases such as the halogens, picogram per second levels could be detected with a selectivity over carbon of about 10^3 but nitrogen and oxygen gave much poorer performance mainly due to the large background signal.

A new version was made commercially available in the 1980s. This version differs from the original in two main respects – firstly the microwave discharge takes place in a cavity at atmospheric pressure and secondly the optical spectrometer is replaced by a photodiode array. The result of these modifications is a detector that is much smaller and easier to operate although the actual performance in terms of sensitivity and selectivity is not greatly different from the original designs. The relative compactness and ease of operation have led to a resurgence of interest in this detector but it is not cheap and as GC-MS systems come down in price they represent strong competition. The definitive account of the various forms of microwave plasma detector is given by de Wit and Beens (see Further Reading).

The Oxygen Selective Detector (O-FID)

The phasing out of lead antiknock compounds in gasoline and their replacement by 'oxygenates' – mainly alcohols and ethers such as methyl tertiary butyl ether (MTBE) – created a need for an oxygen-selective detector, easy to use with capillary columns. The O-FID was first proposed by Schneider in 1982 and is now commercially available. The principle of the detector is that the effluent from the GC column is first passed through a microfurnace made of platinum/rhodium alloy heated to about 1200°C where hydrocarbons are cracked to carbon (which is deposited on the Pt/Rh tubing) and hydrogen. Oxygenated compounds on the other hand form CO which is then passed to a second microreactor with a stream of hydrogen. The microreactor containing nickel deposited on alumina is heated to about 350°C and is small enough to fit into the body of a standard FID. Under these conditions each CO molecule is reduced to a methane molecule so that every oxygen atom in the original effluent peak produces one methane molecule. The whole arrangement sounds complex but it works remarkably well for samples up to 20 μg which is of course satisfactory for capillary columns. The detector is ideally suited for the purpose for which it was designed. **Figure 4** shows an O-FID chromatogram of a gasoline sample containing alcohols, water, ethers and acetone. It should be noted that the detector gives a quite respectable peak from the oxygen in the water.

The disadvantages of the detector are its relatively low concentration sensitivity and linearity compared to other selective detectors and the ordinary FID. The limit of concentration sensitivity is about 0.01%.

Other Element-Selective Detectors

A number of organometallic compounds such as those of tin, lead, arsenic and mercury are readily separated by GC and many more as chelate derivatives. Even such an unlikely element as iron can be dealt with as the volatile chloride, $FeCl_3$, although there are many better methods for such an analysis. For organometallic compounds, atomic absorption and emission spectrometers (AAS and AES), have been used with considerable success. In view of the fact that the vapour emerging from a GC column would appear to be in an ideal state for presentation

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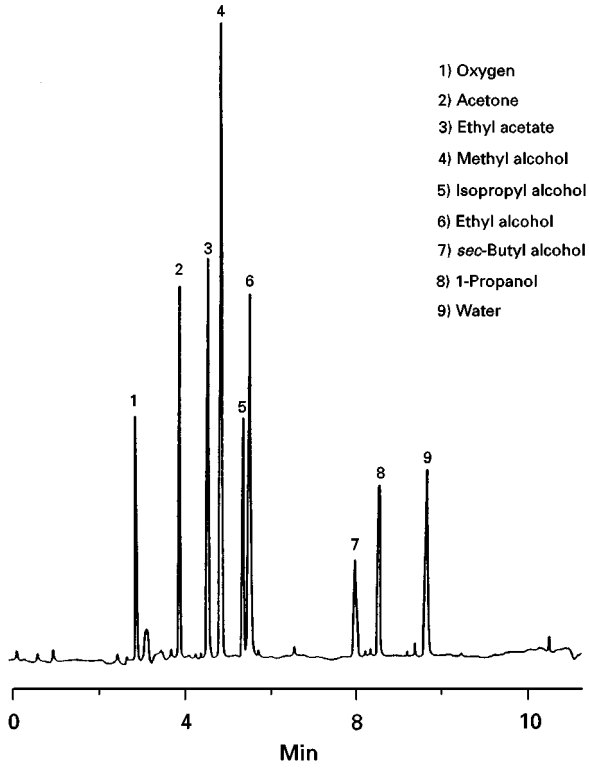

Figure 4 Detection of oxygenates in gasoline at 200 ppm level. (From Sironi, A and Verga, GR. In *Chromatography in the Petroleum Industry* (1995) Adlard, ER (ed.). Reproduced with permission of Elsevier Science Publishers.)

to an AAS it is a little surprising that the technique has not been used more frequently. It has the virtues of high sensitivity for many metals and high selectivity. It also gives information about the speciation of the organometallics which is very difficult to obtain in other ways.

In spite of these advantages relatively little has been published on the use of such detection systems, probably reflecting the relatively minor importance of the analysis of organometallics compared to ordinary organic compounds. Organometallics are, however, important in a number of fields, e.g. the determination of butyltin antifouling paint residues in the environment, and it seems likely that this niche area will remain but not expand significantly in the future.

Compound-Selective Detectors

This category refers to detectors that respond specifically to whole molecules or, more commonly, to various functional groups in a molecule.

An example of a detector responding to functional groups is the automatic titrimeter described by James and Martin in their earliest publications on the separation of the lower fatty acids. Although slow and lacking in sensitivity by modern standards, this detector represented a major advance at the time. Attempts over the years to use microcoulometers as detectors for compounds capable of oxidation or reduction at suitable electrodes have virtually disappeared since, in general, they have slow response and the electrodes are subject of contamination.

Compared to element-selective detectors, there are very few compound-selective detectors and indeed in terms or modern commercially available equipment they can be limited to four – the electron-capture detector (ECD), the photoionization detector (PID) and two spectroscopic detectors, Fourier transform infrared (FTIR) and ultraviolet (UV) detectors. Trapping out polynuclear aromatic hydrocarbon fractions for further analysis by UV spectroscopy was reported many years ago but although there is now an online GC-UV instrument on the market, it is of limited application and will not be discussed further.

The Electron-Capture Detector (ECD)

The development of the ECD by Lovelock in the late 1950s led to its application in environmental studies and the discovery of the wide distribution of chlorinated pesticide residues such as DDT. This was followed by the discovery of the emission of methyl iodide from open ocean waters which again had great significance in the study of the Earth's ecosystem.

The ECD has evolved over many years into an instrument very different in detail from the original even though the principle of detection remains the same. The ionization cross-section detector used a small radioactive source to produce electrons in a cell with two electrodes with about 100 V between them. This caused a small current to flow in the cell as a result of ionization of carrier gas molecules by collision. Compounds eluting from the GC column were ionized to different amounts depending on the cross-section of ionization for each compound. The net result was a variation in the current flowing in the cell which could be recorded electronically. Lovelock modified this detector, firstly by using argon as the carrier gas and secondly by using a much higher voltage (≈ 1000 V) across the electrodes. Under these conditions, multiple ionization takes place via excited argon atoms so that there is a small standing current but a very much larger signal current than given by the cross-section detector. After the argon detector had been on the market for some time, anomalous results were reported especially for halogenated compounds. On investigation, Lovelock concluded that compounds with a strong electron affinity such as polyhalogenated compounds were capturing electrons and thereby reducing the signal

from the detector. He, therefore, maximized the electron capturing effect by using argon with 5–10% methane as carrier gas and about 50 V across the electrodes. Such a cell has a phenomenally high sensitivity for compounds such as CCl_4 and is capable of detecting femtogram quantities (10^{-15} g). Indeed the ECD has a higher sensitivity under favourable conditions than any other detector with the possible exception of radioactivity detectors.

Molecules that capture electrons form charged entities with a much lower mobility than the free electrons responsible for the standing current in the cell. Because of their lower mobility they lose their charge readily and hence cause a reduction in the standing current. The ECD is the only detector that measures a decrease in a large standing current; all other detectors measure an increase in a small standing current. Since the standing current can only be reduced to zero, the ECD can be easily overloaded and has, even in its modern versions, a relatively limited linear range of about 10^4. Modern versions of the ECD pulse the voltage on the electrodes rather than using a steady DC potential. This allows equilibrium to be achieved between the electron flux and the gas mixture in the cell and is somewhat analogous to a distillation column under total reflux from which a small grab sample is removed from time to time. By changing the frequency of the pulses the current in the cell can be kept constant and the variation in frequency required to maintain a constant current is monitored rather than changes in the current itself. This is a very simple arrangement electronically that is readily compatible with integrating circuits. The most recent modification to the ECD dispenses with the radioactive source and uses electrons produced by a helium discharge in an extension to the cell proper.

As indicated in the introduction to this section, the very high sensitivity of the ECD to polyhalogenated compounds made it extremely important for the analysis of trace pesticides in crops since many pesticides were compounds of this type. In addition to a very high sensitivity for some classes of compounds it has a negligible response for others such as paraffin hydrocarbons. **Table 2** shows that the response to different classes of compounds varies over a range of at least 10^6.

This response is not amenable to accurate prediction from the chemical structure of the compounds and even apparently small differences in structure can result in large differences in electron affinity. The ECD is not suitable for detection of an unknown mixture since large peaks may be from small amounts of compounds with high electron affinity or large amounts of compounds with a low electron affinity. In spite of its rather anomalous response and limited linear range, the ECD is an extremely important detector under favourable circumstances.

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The Photoionization Detector (PID)

In the photoionization detector energy sufficient to ionize the compounds emerging from the GC is

Table 2 The electron absorption coefficients of various compounds and of classes of compound for thermal electrons

Electron absorption coefficient[a]	*Compounds and classes*	*Electrophores*
1	Aliphatic saturated, ethenoid, ethinoid and diene hydrocarbons, benzene, and cyclopentadiene	None
1–10	Aliphatic ethers and esters, and naphthalene	None
10–100	Aliphatic alcohols, ketones, aldehydes, amines, nitriles, monofluoro and chloro compounds	•OH•NH_2 •CO• •CN Halogens
100–1000	Enols, oxalate esters, stilbene, azobenzene, acetophenone, dichloro, hexafluoro and monobromo compounds	•CH:C•OH •CO•CO• Halogens
10^3–10^4	Anthracene, anhydrides, benzaldehyde, trichloro compounds, acyl chlorides	CO•O•CO• Phenyl•CO• Halogens
10^4–10^5	Azulene, cyclooctatretrene, cinnamaldehyde, benzophenone, monoiodo, dibromo, tri, and tetrachloro compounds, mononitro compounds	Halogens NO_2 Phenyl•CH:CH•CO•
10^5–10^6	Quinones, 1,2-diketones, fumarate esters, pyruvate esters, diiodo, tribromo, polychloro, and polyfluoro compounds, dinitro compounds	•CO•CO• •CO•CH:CH•CO• Quinone structure Halogens NO_2

Source: After Lovelock. [a]Values are relative to the absorption coefficient of chlorobenzene.

supplied by a small, cheap UV lamp which can be changed over a range of wavelengths to give a certain amount of selectivity. The first commercial detector was designed to operate with packed columns but the large amount of stationary phase bleed from these columns caused rapid fouling of the quartz window of the cell facing the UV lamp and consequent deterioration of performance. Relatively simple design modifications reduced the dead volume to about 40 μL which is adequate for capillary columns of about 0.25 mm i.d. or greater. Use of capillary columns minimizes the fouling from stationary phase and also results in much sharper peaks; since the PID is a concentration-dependent detector this gives a considerable improvement in sensitivity. The main drawback of the commercial PID lies in the UV lamp sources available. Only one gives a single pure wavelength and this is of such low intensity that it offers poor sensitivity. The 10.2 eV lamp emits two wavelengths with an average energy of 10.2 eV. The inhomogeneity of the source blurs the selectivity of the detector although there is no doubt that it gives up to two orders of magnitude greater sensitivity for aromatics over aliphatic compounds with olefins somewhere in between. The lamp of higher wavelength (11.7 eV) is sufficiently energetic to ionize most compounds indiscriminately so the detector fitted with this lamp becomes more or less universal in response. The ideal version of this detector would be one with a tunable laser source and such a detector might rival the mass spectrometer in qualitative information. Unfortunately, the current cost of a tunable laser would render the detector prohibitively expensive and development on these lines is unlikely in the near future.

The FTIR Detector

The main disadvantage of simple mass spectrometry detection is its inability to distinguish between many positional isomers. The technique ideally suited to give such information and the presence of functional groups such as CO and OH is IR spectroscopy. Conventional IR spectroscopy with a grating is too slow for GC purposes but FTIR has the required speed provided that sufficient computing power is available (the computing power required is considerably greater than that required for other techniques). Another disadvantage is that the spectra obtained are gas phase spectra whereas IR spectral libraries have been traditionally liquid phase spectra. The main disadvantages, however, are the wide variation in extinction coefficients, the rather poor sensitivity for many compounds (the upper nanogram range) and light pipe cells with a relatively large dead volume. Since capillary GC seems to be moving in the direction of faster separations via short, very narrow bore capillaries it seems doubtful if GC-FTIR will ever find any great application except perhaps in niche application areas such as essential oil and perfumery analysis.

Conclusion

There still appears to be a place for selective detectors provided that they can offer specific advantages. Early versions of most of the detectors described appeared 30 or more years ago and have survived by constant modifications and improvement in design and performance. In the light of this and the fact that just about every conceivable property of gas mixtures has been exploited over the years it is difficult to envisage any great new advance.

Many detectors have specific advantages for particular applications. The PID only requires one gas supply which makes it suitable for portable equipment. A laboratory monitoring the amount of stenching agents in natural gas is hardly likely to abandon the simplest form of FPD for anything more sophisticated. The ECD reigns supreme in the field of polyhalogenated compounds and the O-FID is ideally suited for the purpose that it was designed for. As speed of analysis increases, detectors are required with very fast response time and low dead volume leading to devices such as time-of-flight mass spectrometers. It would appear that in spite of nearly 50 years of continuous development there is still room for further advances in detectors.

See also: **II/Chromatography: Gas:** Column Technology; Detectors: General (Flame Ionization Detectors and Thermal Conductivity Detectors); Detectors: Mass Spectrometry. **III/Environmental Applications:** Gas Chromatography – Mass Spectrometry. **Fungicides:** Gas Chromatography; **Herbicides:** Gas Chromatography; **Pesticides:** Gas Chromatography; **Petroleum Products:** Gas Chromatography. **Appendix 2: Essential Guides to Method Development in Gas Chromatography.**

Further Reading

Adlard ER (1975) *Critical Reviews in Analytical Chemistry* 5(1): 13–36. (A review of selective detectors up to that date.)

Adlard ER (1995) *Chromatography in the Petroleum Industry*. Amsterdam: Elsevier. (This contains definitive accounts to date on the microwave plasma detector (A de Wit and J Beens), the sulfur chemiluminescence detector (RS Hutte) and the O-FID (A Sironi and GR Verga).)

Brown RA and Searl TD (1979) In: Altgelt KH and Gouw TH (eds) *Chromatography in Petroleum Analysis*. Ch. 13. New York: Marcel Dekker. (An account of early work on offline GC-UV.)

Dressler M (1986) *Selective Gas Chromatography Detectors*. Amsterdam: Elsevier. (A literature survey of most of the selective detectors described up to about 1984. Mainly of historic interest.)

Eicman GA (1990) In: Clement RE (ed.) *Gas Chromatography, Biochemical, Biomedical and Clinical Applications*, Ch. 14. New York: Wiley Interscience. (An account of the GC of organometallic compounds.)

Hill HH and McMinn DG (eds) (1992) *Detectors for Capillary Chromatography*. New York: Wiley Interscience. (An excellent book with chapters on the ELCD (by Hall), the NPD (by Patterson) and GC-FTIR (by Gurka) in particular.)

Gas Chromatography–Infrared Spectrometry

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Knowing the identity of each component in a mixture is necessary for many analytical-scale separations, and simply measuring retention data for this purpose is often too ambiguous for the identification of molecules eluting from a capillary gas chromatography (GC) column, which has the capability of resolving several hundred components. Prior knowledge about the chemical structure of the components and spiking of the mixture with one or more reference standards may aid the identification process; however, a less ambiguous identification can be accomplished by interfacing the chromatograph to a sensitive, rapid-scanning spectrometer to obtain unique signatures of each component. This instrument should allow each component to be detected in real time without any loss in chromatographic resolution. Mass spectrometry (MS) is the most commonly applied technique for this purpose, but it has certain limitations, in particular for distinguishing between structural isomers, such as *ortho*-, *meta*- and *para*-xylene, whose electron-impact and chemical-ionization mass spectra are identical. For such molecules a technique complementary to MS is desired. Fourier transform infrared (FT-IR) spectrometry, which yields unique spectra for most structural isomers, has frequently been used as an alternative technique for this purpose.

DropBooks

Light-Pipe-Based GC-IR Instruments

Measurement of the Spectrum

The coupling of gas chromatographs and FT-IR spectrometers (GC-IR) has been accomplished by three approaches. In the first, and by far the simplest, the GC column is connected directly to a heated flow-through cell. For capillary GC, this cell is usually fabricated from a 10-cm length of heated glass tubing with an internal diameter of $\sim$1 mm. The inside bore of this tube is coated with a thick enough film of gold to be highly reflective to infrared (IR) radiation. IR-transparent windows (for example made of potassium bromide) are attached to both ends of the tube. IR radiation entering one window is multiply reflected down the gold-coated interior bore before emerging from the other window, giving rise to the name *light–pipe* for this device. The effluent from the GC column is passed into one end of the tube and out of the other via heated fused-silica transfer lines. The entire unit is held at a temperature between 250 and 300°C to preclude the condensation of semi-volatile materials.

Infrared radiation from an incandescent source, such as an SiC Globar, is collimated and passed through a rapid-scanning interferometer so that each wavelength in the spectrum is modulated at a different frequency. The beam of radiation is then focused onto the first window of the light-pipe and the infrared beam emerging from the second window is refocused onto a sensitive detector (typically a liquid-nitrogen-cooled mercury cadmium telluride (MCT) photoconductive detector). A typical system is illustrated schematically in **Figure 1**. The signal measured in this way is known as an *interferogram* and the Fourier transform of the interferogram yields a single-beam spectrum. By calculating the ratio of a single-beam spectrum measured when a component is present in the light-pipe to one measured when only the helium carrier gas is present, the transmittance spectrum, $T(\nu)$, of the component is obtained. The transmittance spectrum is usually immediately converted to an absorbance spectrum, $A(\nu)$, by the standard Beer's law operation, $A(\nu) = -\log_{10} T(\nu)$, as the relative intensities of bands in absorbance spectra are independent of the concentration of the analyte, thereby allowing spectral library searching to be